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Phosphorus Speciation Forms in Sewage Sludge from Selected Wastewater Treatment Plants

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1. Introduction

Development of industry and intensive urbanization of the contemporary world constitute one of the greatest threats to humankind and to the natural environment (Bielinska et al. 2014, 2015, Palanisamy & Parthasarathy 2016). Increasing chemical contamination of the environment is caused, among others, by wastewater which often contains numerous harmful substances.

Phosphorus is one of the pollutants found in wastewater. As a nutrient, it infiltrates into the environment from various sources but at the same time is an element essential not only for plants growth and development but also for the existence of all living organisms. Even though it does not occur in the plant and animal cells in very large amounts it constitutes an important element enabling the growth of living organisms.

Phosphorus found in natural waters comes from the erosion of rocks and dissolution of phosphate minerals, erosion of soil – particularly those intensively fertilized with artificial and mineral fertilizers – and discharge of municipal, as well as industrial wastewater along with rainwater. In natural waters, phosphorus is found mainly in the form of orthophosphates. The most common ones occurring in the pH of natural waters include HPO_4^{2-}, H_2PO_4.

The above mentioned wastewater, both municipal and industrial, as well as sewage sludge generated in the wastewater treatment processes constitute significant sources of phosphorus (Szustakowski 2001). Phosphorus contained in sewage sludge may occur in the form of I-, II- and III – univalent, divalent and trivalent metal salts, mainly in the form of magnesium, calcium, iron and aluminum salts. Phosphate salts are characterized by good water solubility, whereas in the case of second- and third-row salts, only the phosphates of alkali metals (except for lithium) are well soluble in water. In sewage sludge phosphorus can be present in the form of phosphates adsorbed on organic and inorganic matter and phosphates characterized by labile bonds with coordination complexes. As a result of numerous processes, certain part of phosphorus is dissolved and may be released to water. The basic factors which influence this process include pH, oxygen content, redox potential, temperature, structure of sludge, its water content, and most of all, the types of chemical compounds in which phosphorus is found (Gomez et al. 1999, Kentzer 2001).

Sewage sludge produced in the course of wastewater treatment process is a valuable source of phosphorus, especially as this element is being rapidly depleted. It is estimated that sources of phosporites will be depleted until 2100, which may lead to a food production crisis (Van Vuuren et. al. 2010, Sattari et.al. 2012, Szaja A. 2013). Therefore, sustainable policy and economy are extremely important (Cholewa & Pawłowski 2009, Pawłowski 2009, 2013, Udo & Pawłowski 2010).

The information which enables to assess the role of sludge as a secondary source of nutrients is the content of biologically available phosphorus, which can be released from sludge and used in the primary production process. In order to determine the content of bioavailable phosphorus, the method of speciation analysis is employed. This analysis aims to determine the phosphorus forms which are of key importance and may be released from sewage sludge (Bezak-Mazur 2004). Previous studies pertained to the quantitative assessment of phosphorus, especially the temporal variability of occurrence of total phosphorus in sewage sludge and its bioavailable forms (Kentzer 2001, Weisz et al. 2000, Golterman 1998). The analysis concerning concentration changes of individual phosphorus forms enables to determine their purpose in the process of releasing this element from sewage sludge.

The information on the chemical form of a given pollutant can be acquired through speciation analysis (Hulanicki 2001). In the speciation analysis of phosphorus contained in the environmental samples the following methods were applied: BCR (Pardo et al. 1998, Ureet al. 1993), Williams (Pardo et al. 1998, Williams et al. 1967) and the Golterman method, which enable binding of various forms of a given element differing in their physico-chemical properties (Pardo et al. 1998, Golterman 1996).

Quantitative profile of phosphorus speciation forms in sewage sludge was determined in the process line of a wastewater treatment plant.

2. Research methodology

Sludge samples acquired from three mechanical-biological treatment plants were used in the study:

Treatment Plant A – employs anaerobic fermentation. The sludge separated in the course of wastewater treatment process in primary settling tank undergoes gravity thickening. Surplus sludge is mechanically thickened on a belt filter press in conjunction with polyelectrolyte. After thickening, the primary and surplus sludge are mixed in appropriate ratio and discharged to separated digesters. Following fermentation, the sludge is directed through gravity thickeners to belt filter presses, where it undergoes the final thickening in conjunction of polyelectrolyte.

Treatment Plant B – employs anaerobic stabilization of sludge in separated digesters, supplied with primary sludge from primary settling tank and sludge from a sequencing batch reactor (SBR) – following prior gravity thickening. At the final stage, digested sludge and polyelectrolyte are directed to centrifuges, where the final dewatering of sludge takes place. In order to chemically precipitate phosphates, iron sulphate is used in the form of PIX coagulant.

Treatment Plant C – employs aerobic stabilization of surplus sludge in the extended aeration process. Thickening of aerobically stabilized sludge takes place in a thickener which is continuously supplied with surplus sludge, directly from the activated sludge basin. Reception of the thickened surplus sludge is adjusted to the operation cycle of mechanical press in which the final dewatering of sludge takes place. In order to chemically precipitate phosphorus compounds, iron sulphate is added in the form of PIX coagulant.

The content of four phosphorus fractions was determined in the acquired sewage sludge with Golterman speciation analysis (Table 1) (Golterman 1988; Golterman 1996).

The speciation analysis was divided into four stages. The first stage was extraction with Ca-EDTA solution over the period of 4 hours. Afterwards, in the second stage, the samples were extracted for 18 hours with Na-EDTA solution. In the next stage, which lasted for 2 hours, extraction was carried out with H_2SO_4. In the final stage, which also took 2 hours, NaOH solution was used. The samples were filtered after each stage, and subsequently subjected to another extraction solvent.The concentration of total phosphorus was determined in the filtrate with spectrophotometric technique, in line with PN. Beforehand, the samplewas oxidized with potassium peroxydisulfate (VI). A spectrophotometer was used for determination.

Table 1. Speciation of heavy metals by Golterman method (Golterman 1988, 1996)
Tabela 1. Specjacja metali ciężkich wg Goltermana (Golterman1988, 1996)

Fraction	Type of extraction solvent and extraction conditions
I. Ca-EDTA-P Phosphorus bonded with hydroxides of iron, aluminium, and manganese	0.05 M Ca-EDTA Extraction time: 4 h
II. Na-EDTA-P Phosphorus bonded with carbonates	0.1 M Na-EDTA Extraction time:18 h
III. H_2SO_4-P Phosphorus associated with organic matter through soluble bonds	0.5 M H_2SO_4 Extraction time:2 h
IV. NaOH-P Remaining phosphorus, also bonded with aluminosilicates and contained in organic matter with bonds unaffected by sulphuric acid in stage III	2 M NaOH Extraction time:2 h

3. Results and discussion

On the basis of speciation analysis carried out with Golterman method on aerobically and anaerobically stabilized surplus sludge samples obtained from three wastewater treatment plants, the prevalence of fraction containing mobile and bioavailable phosphorus can be observed in each case (Fig. 1).

Total share of these fractions (I – Ca-EDTA and II – Na-EDTA) in stabilized sludge from the considered treatment plants amounted to (on average): for plant A – 60%, B – 50%, C – 43%.

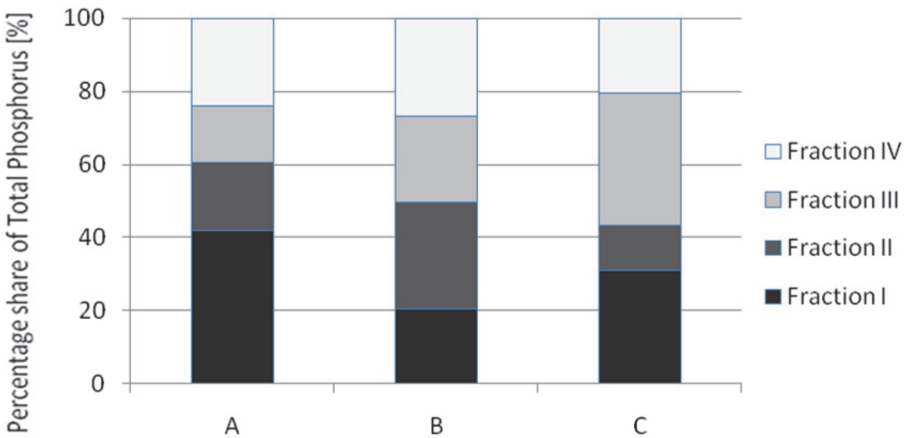

Fig. 1. Percentage share of Total Phosphorus in sludge stabilized in the selected wastewater treatment plants
Rys. 1. Procentowy udział frakcji fosforu ogólnego w osadach stabilizowanych w wybranych oczyszczalniach ścieków

The sequential analysis of sludge separated in primary settling tank of treatment plant C, showed that organic forms of phosphorus (III – H_2SO_4,IV – Na-EDTA) prevailed over the mobile forms, i.e. fraction I and II.

In the samples of primary sludge collected in wastewater treatment plants in which anaerobic fermentation was applied, the total share of mobile forms of phosphorus equals jointly 49% for Plant A and 46% for plant B. In the plant applying the aerobic stabilization the total share of fraction I and II equaled 42% (Fig. 1). The differences between the obtained test results can be explained by the complexity of the primary sludge. In the case of the samples collected from the B- and C-type plants, where the domination of organic forms was observed, such differences can be explained by the actual share of the organic matter in sludge. Similar results were obtained by Professor Bezak-Mazur and Stoińska (Bezak-Mazur, Stoińska 2014).

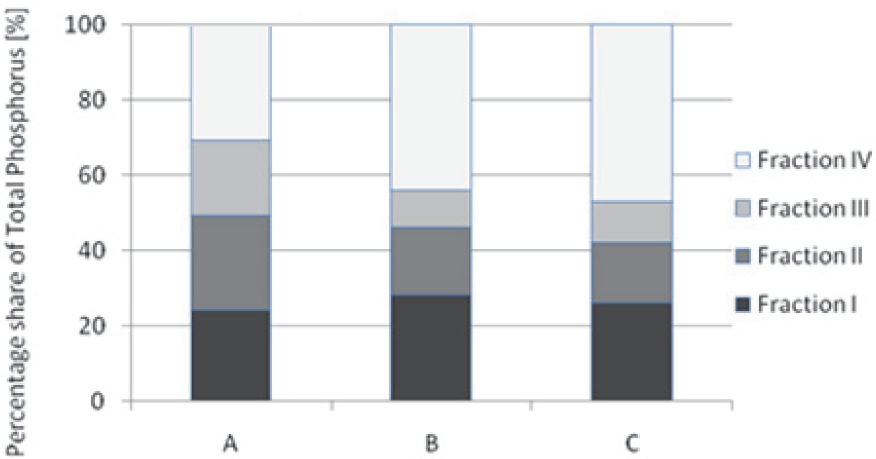

Fig. 2. Percentage share of Total Phosphorus in primary sludge from wastewater treatment plants
Rys. 2. Procentowy udział frakcji fosforu ogólnego w osadach wstępnych pochodzących z oczyszczalniach ścieków

The results of sequential analysis carried out with Golterman method showed the tendency of increasing share of phosphorus in bioavailable fractions along with the consecutive stages of wastewater treatment. In treatment plant C, the total percentage share of mobile phosphorus in the primary sludge equalled 46%, in the activated sludge – 55%, and in the stabilized sludge – 66% (Fig. 3). The observed tendency may result from an increased mineralization of sewage sludge produced in wastewater treatment plants (fractions III and IV bonded with organic matter and aluminosilicates). In these fractions, the total share of phosphorus amounted to 53% for the primary sludge, 45% for the activated sludge, and 34% for the stabilized sludge. Similar data were obtained by Profesor Bezak-Mazur and Stoińska, which confirms the results' repeatability (Bezak-Mazur, Stoińska 2014).

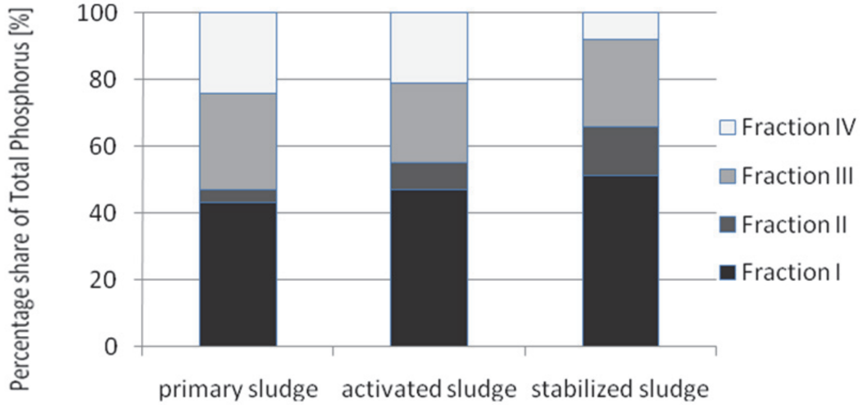

Fig. 3. Percentage share of Total Phosphorus in selected types of sewage sludge produced during treatment in plant C
Rys. 3. Procentowy udział frakcji fosforu ogólnego w wybranych rodzajach osadów ściekowych pochodzących z ciągu oczyszczania oczyszczalni C

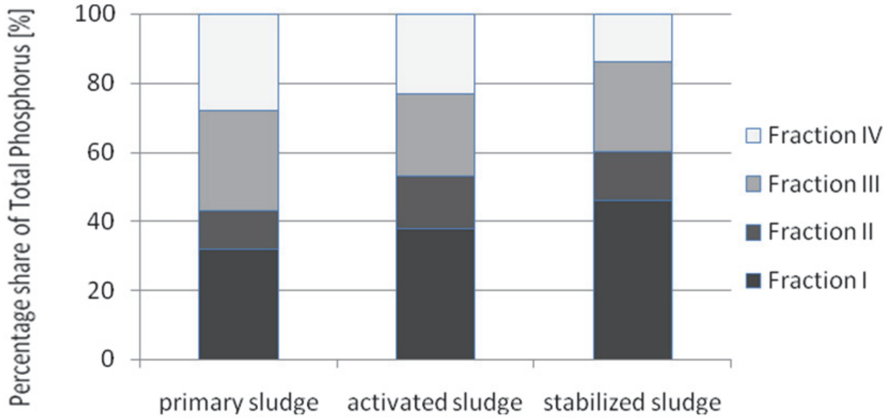

Fig. 4. Percentage share of the fraction of total phosphorus in primary, activated and stabilized sludge produced during the treatment process in plant A
Rys. 4. Procentowy udział frakcji fosforu ogólnego w wybranych rodzajach osadów ściekowych pochodzących z ciągu oczyszczania oczyszczalni A

The obtained results revealed that a significant share of mobile phosphorus in sewage sludge was found in the samples collected from the wastewater treatment plant applying the mechanical-biological-chemical treatment methods (wastewater treatment plant C). However, it was observed that the share of fractions III and IV, related to organic matter, was higher in the sludge samples obtained from plant A than in the samples from plant C. (Fig. 4)

In the phosphorus removal process particular attention should be paid to the appropriate functioning of the secondary sedimentation tank. Holding sludge too long in a tank creates anaerobic conditions which undoubtedly results in the phosphorus release into wastewater.

4. Summary and conclusions

The study presents the tests' results enabling to draw the following conclusions:

- in the analyzed stabilized sludge produced in three wastewater treatment plants the dominating fractions are fractions I and II,
- the sequential analysis of the primary sludge proved the domination of the organic fractions of phosphorus (fractions III and IV) over its mobile forms,
- in the course of wastewater treatment fractions III and IV get reduced in favour of mobile fractions which may be the result of organic matter mineralization,
- the differences concerning the share of particular forms may result from the wastewater treatment technology applied in each of the analyzed wastewater treatment plants as well as from the time for the sludge retention in the secondary sedimentation tank.

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Formy specjacyjne fosforu w osadach ściekowych z wybranych oczyszczalni ścieków

Streszczenie

Urbanizacja oraz rozwój przemysłu to największe zagrożenia dla człowieka i środowiska naturalnego. Jednym z pierwiastków, który z jednej strony powoduje eutrofizację zbiorników wodnych, z drugiej zaś strony jest niezbędnym pierwiastkiem dla rozwoju i życia organizmów żywych jest fosfor. Szacuje się, że przy obecnym poziomie zużycia złóż fosforytów ulegną one wyczerpaniu w ciągu 50-100 lat.

W związku z ciągle wzrastającą liczbą ludności globalne zapotrzebowanie na fosforyty ciągle będzie rosło, dlatego należy poszukiwać metod odzysku tego pierwiastka. O obecnej chwili ponowne wykorzystanie fosforu nie jest powszechnie stosowane, dlatego należy podjąć szybkie kroki do zmiany obecnego stanu. Największe zagrożenie związane z brakiem tego pierwiastka mogą odczuć państwa Unii Europejskiej, gdzie znajdują się niewielkie zasoby tych złóż. Obecna sytuacja zmusza do podjęcia skutecznych działań mających na celu zapobiegniecie wyczerpywania się złóż fosforytów.

Jednym ze źródeł fosforu mogą stać się osady ściekowe. Szacuje się, że 90% fosforu dopływającego do oczyszczalni ścieków odprowadzana jest w osadach ściekowych. Informacją, która pozwoli ocenić osady jako potencjalne źródło fosforu jest to biologicznie dostępna ilość tego pierwiastka. W celu określenia zawartości fosforu biologicznie dostępnego,mającego kluczowe znaczenie, stosuje się metody analizy specjacyjnej.

W pracy określono profil ilościowy form specjacyjnych fosforu w osadach ściekowych powstających w ciągu technologicznym oczyszczalni ścieków. W badaniach wykorzystano osady pochodzące z mechaniczno-biologicznych oczyszczalni ścieków, w których określono metoda Goltermana zawartość fosforu dla wyodrębnionych czterech frakcji. Na podstawie przeprowadzonych badań można stwierdzić, że w ustabilizowanych osadach dominującą jest forma mobilna związana z I i II frakcją. Należy również zauważyć, że formy te zmieniają się w zależności od rodzaju osadów oraz procesów występujących w ciągu technologicznym oczyszczalni ścieków. W osadach: wstępnym, czynnym i nadmiernym łączny udział frakcji mobilnych fosforu wzrasta wraz ze stopniem zmineralizowania.

Słowa kluczowe:
osady ściekowe, fosfor, formy specjacyjne

Keywords:
sewage sludge, phosphorus, speciation forms